

Enrichment of PGE in sulfides: A new insight from Pd solubility in silicate melts

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The platinum-group elements (PGE) are predominantly hosted by sulfides associated with ultramafic layered intrusions (e.g. Merensky Reef, Bushveld Complex; JM Reef, Stillwater Complex). Despite the obvious importance of sulfur and sulfide melts to PGE enrichment processes, our understanding of the role of S in the enrichment of PGE is somewhat scarce. Especially the possible role of S^{2-} as a ligand for PGE in silicate melts is largely unknown. To test the influence of S^{2-} on the PGE solubility in silicate melts, we investigated experimentally the solubility of Pd as a function of oxygen and sulfur fugacities (fO_2 and fS_2 respectively). Therefore a picrite composition was equilibrated with metallic Pd at 1300°C in a 1-atm furnace equipped for gas-mixing. Relative fO_2 conditions ranged from FMQ+1.5 to FMQ-2 and fS_2 was held below FeS saturation. Run products were quenched in air, and subsequently analysed for major elements and dissolved S by electron microprobe, and Pd by LA-ICPMS. In order to avoid overestimation of Pd contents due to nanonugget contamination, only flat parts of the time-resolved laser spectra were quantified.

Initial experiments run under S-free conditions showed that Pd solubility in the natural Fe-bearing melt at low fO_2 roughly resembles the solubility in synthetic Fe-free melts obtained by INAA. This is surprising since bulk analytical techniques, such as INAA, cannot resolve sample heterogeneities and therefore the results may suffer from nanonugget contamination. Moreover, from thermodynamic considerations, the Pd content of the silicate melt is expected to decrease significantly due to the presence of Fe, which is not the case in our experiments.

During S-bearing experiments at an fO_2 of FMQ-1 the metallic Pd reacted with the continuously supplied SO_2 of the gas mixture to form a Pd-S melt. A correction for the presence of Pd-bearing sulfide instead of (Pd,Fe)-alloy is therefore needed to compare the solubility data with S-free systems. Preliminary results indicate that the solubility of Pd in the silicate melt is promoted by the addition of S to the melt. The proportion of Pd associated with the S^{2-} ligand in preference to the more abundant O^{2-} , will be sequestered straight into an exsolving sulfide melt, once sulfide saturation is reached. If the other PGE show the same behaviour it will have profound implications to our current models for PGE enrichment processes in sulfide bearing ultramafic layered intrusions.

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